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DIELS-ALDER AND ENE REACTIONS OF NITROSYL HYDRIDE AND NITROSOFORMALDEHYDE

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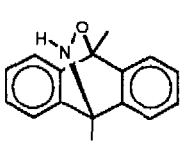
Abstract: Nitrosyl hydride and nitrosoformaldehyde have been prepared by the thermolysis of their 9,10-dimethylanthracene adducts. Both HNO and HCONO are found to be reactive as enophiles and dienophiles.

Nitrosyl hydride or nitroxyl (HNO) has been the subject of numerous theoretical studies[1] and has been extensively studied in the gas phase.[2] HNO has been proposed as an intermediate in the combustion of nitrogeneous substances[3] and has been detected as a constituent of interstellar clouds.[4] However, we are aware of no reports of the solution reactions of HNO other than dimerization followed by decomposition to water and N_2O.[2b] Kirby has reported the conversion of **2** to **1** by methoxide catalyzed hydrolysis, treatment with anhydrous HCl, purification of the hydrochloride salt of **1** and liberation of the free amine by treatment with base.[5] Kirby observed the microwave spectrum of free HNO on thermolysis of **1** at 70-100°C. We have used a modification of Kirby's method for the direct conversion of **3** to **1**.



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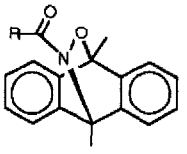
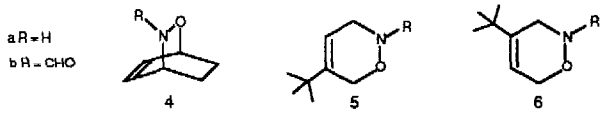


2 R = CH_3 or C_6H_5
3 R = H

The periodate oxidation of formylhydroxamic acid[6] in the presence of 9,10-dimethylanthracene gives the formylnitroso-9,10-DMA adduct **3** in 95% yield.[7] Treatment of an ethanolic solution of **3** with anhydrous ammonia followed by evaporation of the solvent affords an 80% yield of **1**[8] which is contaminated with small quantities of 9,10-DMA.

Because of our interest in the chemistry of singlet oxygen we have investigated the reactions of nitrosyl hydride with substrates which react readily with singlet oxygen. Singlet oxygen reacts with conjugated 1,3-dienes in a 4+2 fashion to afford cyclic endoperoxides and undergoes ene reactions with olefins to produce allylic hydroperoxides.[9]

Compound 1 undergoes smooth thermal decomposition to HNO and 9,10-DMA in refluxing benzene or THF. The liberated HNO can be trapped with 1,3-cyclohexadiene (2 equiv., refluxing THF, 1 hr.) to give the known[10] 4+2 adduct **4a** in 47% yield.[8] Similarly, the generation of HNO in the presence of 2 equivalents of 2-t-butylbutadiene gives a 56% yield of a 3:2 mixture of the Diels-Alder products **5a** and **6a**, respectively.[8] The regiochemistry of the 4+2 adduct could not be unambiguously assigned by examination of the NMR spectra of **5a** and **6a**, but was determined by



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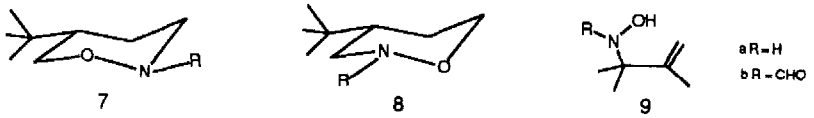
correlation with **5b** and **6b** as described below. The thermal decomposition of **1** in the presence of 2 equivalents of tetramethylethylene affords the allylic hydroxylamine derivative **9a** in 80% yield.[8]

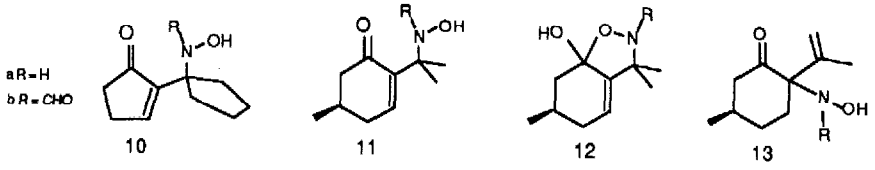


7 8 9

Dailey and coworkers have recently proposed nitrosoformaldehyde as a possible intermediate in the decomposition of nitrocarbene; however, they were unable to trap the proposed intermediate.[11] Since compound **3** promised to be a convenient precursor to nitrosoformaldhyde, we investigated its trapping efficiency with various olefins and dienes. Compound **3** is considerably more thermally stable than **1** or previously reported acylnitroso-9,10-DMA adducts;[12] therefore, the liberation of nitrosoformaldehyde is routinely conducted in toluene at reflux. Under these conditions reaction of **3** with 1,3-cyclohexadiene (2 equiv., refluxing toluene, 2 hrs) gives a 90% yield of **4b**[8] and reaction with 2 equivalents of 2-t-butylbutadiene gives a 7:1 mixture of **5b**:**6b**,[8] respectively, in 95% yield. Ammonolysis of the mixture of **5b:6b** (EtOH, anhydrous ammonia) gave a 7:1 mixture of **5a** and **6a**, respectively. Again, the regiochemistry of the 4+2 cycloaddition was not evident from examination of the NMR spectra of the mixture of **5b** and **6b**, but it was determined by conversion (H_2, PtO_2, EtOH, HOAc) to a 7:1 mixture of **7b** and **8b**[8] where structure determination was possible. Thermal decomposition of **3** in the presence of 2 equivalents of tetramethylethylene gives the ene adduct **9b** in 62% yield.[8]

In connection with our studies of the reaction of singlet oxygen with α,β-unsaturated ketones[13] we have studied the reaction of HNO and HCONO with cyclopentylidenecyclopentanone and R-(+)-pulegone. Compound **1** reacts with 1.2 equivalents of cyclopentylidenecyclopentanone by abstraction of a β'-hydrogen atom to give a β-hydroxylamino-α,β'-enone **10a**[9] in 60% isolated yield. Reaction of compound **1** with 1.2 equivalents of R(+) pulegone results in exclusive β'

hydrogen atom abstraction to give a 54% yield of **11a** which is in equilibrium (4:1 respectively) with its cyclic hemiacetal, **12a**.[8] Similar to compound **1**, **3** reacts with 1.2 equivalents of cyclopentylidenecyclopentanone to give exclusively (90% yield) the ketohydroxamic acid, **10b**.[8] However, the reaction of **3** with (+)-pulegone is not nearly so clean. At least five different products are formed which include the conjugated enones **11b** and **12b** and also **13** as a mixture of the two disasteriomers.



10 11 12 13

We are continuing to study the similarity of reactivity patterns between singlet oxygen and HNO.

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7. To 2.44 mmol of 9,10-DMA and 4.88 mmol of $\phi CH_2N^+(CH_3)_3\ IO_4^-$ in 7 ml of DMF was added a solution of 4.88 mmol of HCONHOH in 2 ml of DMF. After 30 min at RT the precipitated **3** was filtered and washed with a small amount of cold benzene.
8. All new compounds gave satisfactory elemental analysis. Spectra for selected compounds follow: For **1**: PMR ($CDCl_3$) δ 2.02 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 5.09 (bs, 1H, NH), 7.20-7.28 (m, 4H, aromatic), 7.31-7.38 (m, 4H, aromatic); CMR($CDCl_3$)δ 14.00, 15.05,

57.89, 76.67, 120.46 (2C), 126.69, 126.96, 140.44, 142.26. For **3**: PMR ($CDCl_3$) δ 2.29 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 7.2-7.5 (m, 8H, aromatic), 8.22 (s, 1H, HCO); CMR ($CDCl_3$) δ 14.60, 14.65, 62.06, 80.10, 120.05, 121.17, 127.78 (2C), 140.08, 141.04, 152.90. For **4a**: PMR ($CDCl_3$) δ 1.3 (m, 2H, CH_2), 1.9 (m, 2H, CH_2), 3.67 (m, 2H, NCCH), 4.46 (m, 2H, OCCH), 6.50 (m, 2H, vinyl); CMR ($CDCl_3$) δ 20.03, 24.54, 49.36, 67.87, 130.93, 132.78. For **5a** (major product): oil, PMR ($CDCl_3$) δ 1.01 (s, 9H, $C(CH_3)_3$), 3.54 (m, 2H, CH_2N), 4.28 (m, 2H, CH_2O), 5.6 (m, 1H, vinylic); CMR ($CDCl_3$) δ 28.78, 33.92, 47.27, 67.84, 114.64, 144.31. For **5b** (major product): oil, PMR ($CDCl_3$) δ 1.0 (s, 9H, $C(CH_3)_3$), 4.14 (m, 2H, CH_2N), 4.47 (m, 2H, CH_2O), 5.5 (m, 1H, vinylic), 8.4 (s, 1H, HCO); CMR ($CDCl_3$) δ 28.63, 34.11, 40.67, 71.39, 112.32, 143.36, 160.55. For **7b**: PMR ($CDCl_3$) δ 0.84 (s, 9H, $C(CH_3)_3$), 1.1-1.35 (m, 1H, CH), 1.35-1.6 (m, 2H, CH_2), 3.01 (dt, J = 3.5 Hz, J = 13.5 Hz, 1H, ax NCH), 3.56 (app. t, J = 10.5 Hz, 1H, ax OCH), 4.18 (bd, J = 10.5 Hz, 1H, eq OCH), 4.34 (dd, J = 3.5 Hz, J = 13.5 Hz, 1H, eq NCH), 8.32 (s, 1H, CHO); CMR ($CDCl_3$) δ 23.49, 26.89, 30.91, 40.96, 44.21, 75.99, 159.55. For **9a**: PMR ($CDCl_3$) δ 1.21 (s, 6H, CH_3), 1.77 (d, J = 0.7 Hz, 3H, CH_3), 4.9 (bs, 2H, vinyl); CMR ($CDCl_3$) δ 19.24, 24.25, 61.06, 111.74, 148.91. For **9b**: PMR ($CDCl_3$) 1.5 (s, 6H, CH_3), 1.72 (s, 3H, CH_3), 5.0 (bs, 2H, vinyl), 8.07 (s, 1H, CHO); CMR ($CDCl_3$) δ 18.49, 25.11, 64.16, 113.18, 146.16, 154.63. For **10a**: mp 78-80°C; PMR ($CDCl_3$) δ 1.5-2.0 (m, 8H, CH_2), 2.4 (m, 2H, CH_2), 2.56 (m, 2H, CH_2), 5.7 (bs, 2H, NH, OH), 7.43 (t, J = 2.8 Hz, 1H, vinyl); CMR ($CDCl_3$) δ 23.98, 26.02, 34.24, 35.48, 66.44, 148.16, 158.59, 209.83. For **10b**: mp 90-92°C; PMR ($CDCl_3$) δ 1.5-2.6 (m, 12H, CH_2), 7.5 (t, J = 2.6 Hz, 1H, vinyl), 8.29 (s, 1H, HCO); CMR ($CDCl_3$) δ 22.06, 22.19, 25.91, 34.08, 35.61, 144.59, 156.33, 160.46, 207.39. For **11a**: PMR ($CDCl_3$) δ 1.0 (d, J = 7 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 2.1 (m, 3H, CH_2 and CH), 2.47 (m, 2H, CH_2), 6.83 (m, 1H, vinyl); CMR ($CDCl_3$) δ 20.89, 24.56, 30.08, 34.58, 47.77, 59.92, 141.35, 145.91, 200.1.

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